BEITRÄGE ZUR KENNTNIS DER ALLOTROPEN MODIFIKATIONEN VON SCHWEFEL.[1]

I. ZUR KRYOSKOPIE DES SCHWEFELS.

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Die leichte Umwandlung in allotrope Modifikationen lässt den Schwefel als wenig geeignet erscheinen, um als Lösungsmittel bei kryoskopischen Versuchen Anwendung zu finden. Bei 119.25° schmelzender, monokliner Schwefel weist nach 6–8 stündigem Erhitzen bei der genannten Temperatur einen Erstarrungspunkt von 114.5°, also um 4.75° niedriger, auf, da offenbar eine oder mehrere neue Modifikationen entstehen, welche den Schmelzpunkt in gleicher Weise herabsetzen wie irgend ein fremder in Schwefel löslicher Stoff. Auch der Erstarrungspunkt von 114.5° ist nicht unveränderlich, sondern unterliegt mit Änderung der Aussenbadtemperatur entsprechenden Schwankungen. Wird die letztere erhöht, so tritt weitere Erniedrigung ein. Will man also möglichste Konstanz und Einheitlichkeit des Schmelzpunktes erreichen, so muss das Schmelzen in Badtemperaturen erfolgen, welche gerade über dem Schmelzpunkt des jeweilig bestehenden Gleichgewichts liegen, und umgekehrt darf das Erstarren nur bei Temperaturen, die gerade unter dem Gefrierpunkt des jeweilig bestehenden Gleichgewichts liegt, herbeigeführt werden.

Solche Versuche setzen voraus Konstanz der eingestellten Badtemperatur sowie die Möglichkeit, schnelle Änderungen dieser vorzunehmen, wenn Schmelzen oder Erstarren bewirkt werden sollen. Dampfbäder, die diesen Voraussetzungen sehr vollkommen entsprechen, sind die von E. Beckmann, W. Weber und O. Liesche[2] konstruierten Manostaten, bei denen die Badtemperatur einmal unabhängig von der Aussentemperatur ist, zum andern tagelang innerhalb einiger hundertstel Grade konstant erhalten werden kann.

Bei der für flüssigen Schwefel (110–125°) in Betracht kommenden Temperatur erwies sich Gärungsamylalkohol (Sp. 132°, 760 mm.) als Dampfbad besonders geeignet, da nur mit Hilfe einer gewöhnlichen an den Manostaten angeschlossenen Wasserstrahlluftpumpe die Siedetemperatur von 132° entsprechend herabgesetzt zu werden brauchte.

Um überhaupt eine Kryoskopie des Schwefels aufbauen zu können,

(1) Ausführung dieser Versuche im Kaiser Wilhelm Institut für Chemie, Berlin-Dahlem auf Anregung und unter Leitung von Prof. Dr. E. Beckmann†.

(2) *Z. physik. Chem.*, **79** (1912), 565; **88** (1914), 13.

kam nur der natürliche Schmelzpunkt von 114.5° als Grundlage der Versuche in Frage. Der aus Schwefelkohlenstoff auskristallisierte und von diesem im Vakuum völlig befreite Schwefel wurde zunächst im Gefrierrohr durch den Manostaten auf eine Temperatur von 121° geschmolzen, die anfängliche bei 119° liegende Erstarrungstemperatur senkte sich mit der Zeit auf 114.5°.

Die Erstarrungstemperatur wurde ermittelt durch langsames Erniedrigen der Badtemperatur bei gleichzeitigem ständigen elektromagnetischen Rühren,[1] worauf durch das Einbringen eines $2\frac{1}{2}$ mm. starken Platindrahts von Zimmertemperatur durch Wärmeentziehung Erstarren erfolgte.

Auf die Badtemperatur war besonders deswegen stets sorgfältig zu achten, weil bei der geringen latenten Schmelzwärme des Schwefels und der hoch viskosen Beschaffenheit der Schmelze der Wärmeausgleich zwischen Flüssigkeit und Kristallen nur langsam eintritt. Ist die Temperaturdifferenz zwischen Gefrierrohr und Bad zu gross, so wird die Ablesung der Gefriertemperatur leicht fehlerhaft.

Während in den folgenden Tabellen die Badtemperaturen sich auf Ablesungen am Normalthermometer bezeichen, sind die Erstarrungspunkte des Schwefels als direkte Ablesungen am Beckmannthermometer aufgeführt.

Die ersten Versuchsserien sollen zeigen, dass es bei Erhitzen über Nacht gelingt, ein festes Gleichgewichtsverhältnis herzustellen, dass also die Erstarrungspunkte im Rahmen experimenteller Fehlergrenzen Konstant bleiben.

Versuchsserie	Badtemperatur beim Schmelzen	Normalthermometer beim Erstarren	Zeit min.	Erstarrungspunkt Beckmannthermometer
I a	116	114	0	2.485
I b	116	114	25	2.467
I c	116	114	50	2.481
II a	116	114	0	3.838
II b	116	114	15	3.843
II c	116	114	30	3.841
III a	116–117	114	0	3.631
III b	116	114	20	3.630
III c	116	114	40	3.633

(1) *Z. physik. Chem.*, **21** (1896), 241.

Um das Gleichgewichtsverhältnis in kürzerer Frist zu erreichen, wurde Schwefel in einem Aussenbad von 180° (siedendes Anilin) erhitzt und alsdann auf 115–116° abgekühlt, wobei das Wiederansteigen der Temperatur kryoskopisch geprüft wurde.

Versuchsserie	Badtemperatur beim Schmelzen	Normalthermometer beim Erstarren	Zeit min.	Erstarrungspunkt Beckmannthermometer
IV a	115.0	113.0	0	2.667
IV b	115.2	113.2	20	2.868
IV c	115.4	113.4	35	2.945
IV d	115.6	113.6	50	3.074
IV e	115.6	114.0	210	3.585
IV f	116.0	114.0	225	3.580
IV g	116.0	114.0	237	3.586

Solchermassen liess sich also in 3–4 Stunden Konstanz des Erstarrungspunkts erreichen. Diese Frist lässt sich auf 2 Stunden kürzen, wenn man zunächst den Schwefel 75 Minuten lang auf 140° in Dampf von siedendem *m*-Xylol erhitzt und ihn dann der Badtemperatur von 116° aussetzt.

Eine weitere Möglichkeit, die Konstanz zu beurteilen, besteht in der nach Smith[1] ermittelten Entstehung von amorphem, in Schwefelkohlenstoff unlöslichen Menge an Schwefel (S_μ), die als Ursache des um 4.75° mit der Zeit sinkenden Erstarrungspunktes für 114.5° 3.6% betragen soll und deren Bestimmung dergestalt erfolgt, dass die Schmelze in eine kalte Porzellanschale ausgegossen und nach 24 Stunden mit Schwefelkohlenstoff extrahiert wird. Bei verschieden langem Erhitzen auf 140° ergaben Versuche folgenden Gehalt für S_μ:

1 Stunde 2.31%
1 1/4 Stunden 3.56%
1 1/2 Stunden 4.20%
1 3/4 Stunden . . . . . 6.90%.

Unter Berücksichtigung des von Smith angegebenen Werts von 3.6% S_μ für den natürlichen Schmelzpunkt von 114.5° war es also zweckmässig, wie oben angegeben, 1 1/4 Stunden zu erhitzen.

Wurden Beckmann- und Normalthermometer bei Gleichgewichtszustand miteinander verglichen, so ergaben sich folgende absolute Schmelzpunkte:

(1) *Z. physik. Chem.*, **42** (1903), 469.

Badtemperatur	Erstarrungspunkt
115.18°	114.3°
115.31	114.4

Die erhaltenen Werte befinden sich mit den Angaben von Smith in Übereinstimmung, die Brauchbarkeit des natürlichen Schmelzpunkts als Grundlage für kryoskopische Versuche war demnach nicht zu bezweifeln.

Es blieb lediglich zu prüfen, ob das Gleichgewicht durch lösen fremder Stoffe verändert werde oder im wesentlichen erhalten bleibe. Im letzteren Falle mussten bei verschiedenen Stoffen übereinstimmende molekulare Erniedrigungen erhalten werden. Mit Rücksicht auf Löslichkeit, chemische Indifferenz, sowie Kenntnis der molekularen Assoziations-bezw. Dissoziationsverhältnisse wurden zunachst organische Stoffe und zwar nacheinander:

1. Naphtalin
2. Diphenyl
3. β-Naphthol
4. α-Naphtholsäure
5. Thymol
6. *p*-Kresol
7. Chinolin
8. Anilin
9. Phenylsenföl
10. α-Thiophencarbonsäure
11. Bromoform

gewählt.

Diese Versuche ergaben folgendes tabellarisch, zusammengestelltes Bild:

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	K
1. Gelöst Naphtalin, $C_{10}H_8=128$.					
27.11	0.0287	0.202	112.2	115.0	244.2
	0.0500	0.269	111.8	114.8	186.7
	0.0559	0.349	111.6	114.5	206.6
	0.0431	0.254	111.3	114.2	214.5
				Mittel	213.0
25.12	0.0655	0.485	113.5	116.0	238.1
	0.0848	0.566	112.9	115.5	214.6
	0.0718	0.434	112.4	114.9	194.4
	0.0630	0.376	112.0	114.4	191.9
				Mittel	209.8

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	K
2. Gelöst Diphenyl $C_{12}H_{10}=154.1$.					
25.00	0.1119	0.620	113.5	115.5	213.5
	0.1179	0.607	112.9	114.9	198.3
	0.1165	0.645	112.2	114.3	213.3
	0.1391	0.678	111.5	113.5	187.8
	0.0824	0.401	110.8	112.8	187.5
				Mittel	200.1
25.00	0.1289	0.774	113.3	116.0	231.3
	0.1529	0.839	112.4	115.2	212.0
	0.1326	0.711	111.6	114.4	206.6
				Mittel	216.6
3. Gelöst β-Naphthol $C_{10}H_7OH=144.1$.					
25.00	0.0873	0.547	113.5	116.0	225.7
	0.0897	0.530	112.9	115.4	212.9
	0.0996	0.589	112.4	114.8	176.9
				Mittel	205.2
4. Gelöst α-Naphtholsäure $C_{10}H_7COOH=172.1$.					
25.00	0.0539	0.225	113.7	116.0	179.6
	0.0365	0.143	113.5	115.7	168.6
	0.0629	0.123	113.2	115.5	184.1

Die schwere Löslichkeit der Substanz und die abnorm niedrigen Konstanten lassen in diesem Falle deutlich Assoziation der Säuremoleküle erkennen.

5. Gelöst Thymol $C_{10}H_{13}OH=150.1$.					
25.00	0.0765	0.425	113.6	116.0	208.5
	0.0579	0.337	113.2	115.6	218.4
	0.0629	0.352	112.8	115.2	210.0
				Mittel	212.3
25.00	0.0705	0.395	113.6	115.5	210.2
	0.0731	0.394	113.2	115.2	202.3
	0.0711	0.358	112.8	114.8	188.9
				Mittel	200.5

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	K
		6. Gelöst *p*-Kresol $C_7H_7OH=108.1$.			
25.00	0.0840	0.648	113.7	116.0	208.4
	0.1658	1.165	112.5	115.4	189.8
	0.1548	0.871	111.4	114.2	136.3 (!)
				Mittel	178.1
25.00	0.0850	0.618	113.4	116.0	196.5
	0.0822	0.578	112.7	115.4	189.9
	0.0909	0.528	112.2	114.8	156.8
				Mittel	181.1
		7. Gelöst Chinolin $C_9H_7N=129.1$.			
25.00	0.0881	0.591	113.6	116.0	215.8
	0.1145	0.777	112.8	115.4	219.0
	0.1142	0.685	112.0	114.6	193.6
				Mittel	209.5
		8. Gelöst Anilin $C_6H_5NH_2=93.1$.			
25.00	0.1038	0.970	113.4	115.7	217.5
	0.1074	0.927	112.4	114.8	200.9
	0.1061	0.853	111.5	113.8	187.1
				Mittel	201.8
		9. Gelöst Phenylsenföl $C_6H_5NCS=135.2$.			
25.00	0.1416	0.982	113.2	115.6	234.4
	0.1093	0.763	112.3	114.6	236.0
	0.1157	0.729	111.5	113.9	213.0
				Mittel	227.8
25.00	0.0974	0.695	113.3	115.7	241.2
	0.1015	0.702	112.6	115.0	233.8
	0.1009	0.665	111.9	114.3	222.8
	0.1032	0.623	111.2	113.6	204.0
				Mittel	225.5

Schwefel in gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	K
10. Gelöst α-Thiophencarbonsäure $C_4H_3SCOOH=128.1$.					
25.00	0.0981	0.467	113.3	115.3	152.5
	0.1001	0.329	113.0	114.8	105.3
	0.0987	0.307	112.6	114.5	99.6
				Mittel	119.1
25.00	0.0978	0.449	113.5	115.5	147.0
	0.0997	0.390	113.1	115.0	125.0
	0.0999	0.319	112.7	114.6	102.3
				Mittel	124.7

Wie bei der Verwendung von α-Naphtholsäure scheint auch in diesem Falle das Ergebnis auf eine Assoziation der Säuremoleküle hinzudenken.

11. Gelöst Bromoform $CHBr_3=252.9$.					
25.00	0.1958	0.637	113.2	115.5	205.7
	0.1602	0.592	112.5	115.0	233.6
	0.2533	0.910	111.8	114.5	227.1
				Mittel	222.1
25.00	0.1579	0.573	113.5	116.0	229.4
	0.1801	0.692	112.8	115.5	242.9
	0.1669	0.618	112.2	114.8	234.1
				Mittel	235.5
25.00	0.1872	0.705	113.2	115.0	238.1
	0.1866	0.653	112.5	114.2	221.3
	0.1655	0.623	111.9	113.5	238.0
	0.2071	0.733	111.0	112.8	223.8
				Mittel	230.3

Nach der Höhe ordnen sich die Konstanten folgendermassen:

Bromoform (11)	229.3
Phenylsenföl (9)	226.6
Naphtalin (1)	211.4
Diphenyl (2)	208.4
Thymol (5)	206.4
Chinolin (7)	205.7
β-Naphthol (3)	205.2

Anilin (8) 201.8
p-Kresol (6) 208–136
α-Naphtolsäure (4) 179–168.6
α-Thiophencarbonsäure (10). . . 152.5–102.3

Sieht man von den letzten drei Substanzen ab, deren Konstanten bei steigender Konzentration der Lösung stark abfallen, was auf den Gehalt an Hydroxyl und die Neigung zur Assoziation in dem nur schwach dissoziierenden Schwefel mit der kleinen Dielektrizitätskonstante 4.0 zurückgeführt werden darf, so erhält man für die übrigen Körper eine kryoskopische Konstante von im Mittel mit K=213.

Aus dieser berechnet sich die latente Schmelzwärme nach der van't Hoffschen Formel:

$$w = \frac{0.02 \times T^2}{K} = 14.1 \text{ gr.-Kal.}$$

im Gegensatz zu den bisher bekannten Werten für die Schmelzwärme des monoklinen Schwefels, die zwischen 9.368 und 12.5 gr.-Kal. schwankten.

Von besonderem Interesse erschien nach Ermittlung der Konstante K=213, das Molekulargewicht der analytisch viel verwendeten unlöslichen Sulfide zu bestimmen, obwohl gerade deren Löslichkeit in Schwefel beim natürlichen Schmelzpunkt nicht sehr gross ist.

Die zunächst mit Arsentrisulfid (As_2S_3=246.2) ausgeführten Versuche ergaben folgendes Resultat:

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	Mol. Gew. (K=213)	Mol. As_2S_3
25	0.0530	0.194	113.5	116.0	233	0.95
	0.0510	0.096	113.5	115.8	457	1.86
	0.0534	0.077	113.5	115.7	591	2.40
25	0.0540	0.194	113.8	116.0	309	1.25
	0.0364	0.070	113.7	115.8	443	1.80
25	0.0686	0.185	113.8	115.8	316	1.28
	0.0677	0.107	113.7	115.7	539	2.19

Die in sehr verdünnter Lösung vorhandenen Einzelmoleküle haben bei steigender Konzentration offenbar die Tendenz zur Polymerisierung.

Da weiter das Molekulargewicht von Selentetrachlorid experimentell noch nicht einwandfrei bestimmt wurde, erschien auch hiermit ein Versuch

in Schwefel als kryoskopischem Lösungsmittel naheliegend, wobei sich folgendes Resultat ergab:

Schwefel gr.	Gelöst, gr. Einzelmengen	Erniedrigung in °C.	Badtemperatur beim Erstarren	Badtemperatur beim Schmelzen	Mol. Gew. (K=213)	Mol. bezogen auf $SeCl_4$
25	0.1126	0.687	113.5	115.7	139.6	0.63
	0.1013	0.769	112.8	115.0	112.2	0.51
	0.1031	0.767	112.0	114.2	114.5	0.52
25	0.0894	0.511	113.3	115.6	149.1	0.67
	0.1106	0.862	112.8	115.1	109.3	0.49
	0.1137	0.948	111.9	114.2	102.1	0.46

Da das Molekulargewicht nur etwa halb so gross gefunden wurde, wie es der normalen Formel $SeCl_4=220.9$ entsprechen würde, hat das Selentetrachlorid offenbar auf den Schwefel wie folgt reagiert:

$$\underset{(2\text{ mol})}{2SeCl_4+6S} = \underbrace{Se_2Cl_2+3S_2Cl_2}_{(4\text{ mol})}$$

Zusammenfassung.

1. Beim natürlichen Schmelzpunkt 114.5° des Schwefels sind mit einer Reihe organischer Substanzen die kryoskopischen Konstanten des Schwefels bestimmt worden, wobei ein mittlerer Wert von K=213 resultierte, der einer latenten Schmelzwärme von 14.1 gr.-Kal. entspricht.

2. Auf Grund seiner kleinen Dielektrizitätskonstante besitzt der Schwefel nur geringe dissoziierende Kraft und lässt bei Säuren die Neigung zur Bildung von Doppelmolekülen erkennen.

3. Arsentrisulfid zeigte in verdünnten Lösungen Moleküle As_2S_3, während bei konzentrierteren Polymerisierung eintrat.

4. Selentetrachlorid ergab das halbe normale Molekulargewicht auf Grund der Bildung von Selenchlorür und Schwefelchlorür.

In einer zweiten Abhandlung sollen auf flüssigen Schwefel einwirkende katalytische Einflüsse behandelt werden, während die letzte Arbeit sich mit den Beziehungen von Jod zu Schwefel und Selen befassen soll.

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SINOMENINE AND DISINOMENINE. PART XI. ON THE POSITION OF THE DOUBLE LINKING IN SINOMENINE.

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In Part X of this communication, the following three reasons were given in assigning C_7-C_8 position to the double linking of sinomenine.

1. The easy reducibleness of the double linking with nascent hydrogen.

2. The easy hydrolysis of the methoxylgroup, which situates on C_7, by the heating with dilute hydrochloric acid and the after-treatment with ammonia, viz., the formation of bis-[demethyl]-sinomenyliden.

3. The linking together of two sinomenine molecules by the reduction with Na-amalgam.

In the present paper, these three points, together with the formation of d-form of Speyer's dihydrothebainone, already mentioned, will be given in a detailed manner.

I.

When sinomenine is reduced with Na-amalgam in a dilute caustic soda solution, a substance $(C_{18}H_{22}NO_3)_2$ is formed in a 60% yield, besides a small quantity of a substance which is very similar to the desmethoxy-dihydro-sinomenine. (See section II).

The substance $(C_{18}H_{22}NO_3)_2$ has a great tendency to crystallize and it forms beautiful prisms in the course of the evaporation of its chloroform solution. As is given in Table 1, it melts at 304°, and has a double molecular weight. It has only two methoxyls, thus one methoxyl group of each sinomenine molecule being reduced away. It retains the original keton group and forms a disemicarbazone. The ferric chloride reaction and diazo-reaction are also retained in an undiminished degree.

Table 1.

$(C_{18}H_{22}NO_3)_2$	
Yield	ca. 60% (raw)
M. p.	304° (commonly 294°)
Crystal form	stout prisms
Mol. wt.	626 (calc. 600)
$[\alpha]_D$	−24.49°
M. p. of iodomethylate	>300°
M. p. semicarbazone	>300°
Methoxyls	two
$FeCl_3$-reaction	+in alcohol
Diazo-reaction	+in 2,500,000th dilution
$K_3Fe(CN)_6$-reaction	purple
Formaline-SO_4H_2	pure blue

As to the linking point of two sinomenine molecules in this substance, 1, 1′-position is excluded, since this substance gives diazoreaction in the same degree as sinomenine itself (disinomenine and ψ-disinomenine give the diazoreaction in a slightest degree).[1] The pinacone linking is also out of question, as the new substance forms a disemicarbazone and more especially, dihydrosinomenine does not give any double molecular substance by the reduction.

The formation of this double molecular compound can therefore only be explained by the parallelism with the reduction of the benzalacetone.

Harries and Muller[2] obtained, in 1902, a diphenyl-octadione by reducing benzal-acetone, and thus showed that α, ß-unsaturated ketone can be linked together by Na-amalgam reduction. The linking point was afterwards more thoroughly determined to be β-position to the ketone group with coumaline by Asahina and Shibata.[3]

From these considerations, it is most reasonable to assume that two melecules of sinomenine was linked together in the β—position to the keton group and that the double linking of the sinomenine must be conjugated to the keton group. This assumption is enforced through the fact that the double linking is reduced by the simple zinc dust and hydrochloric acid couple.

It is a difficult problem to determine whether the position of the ethanamine chain was dislocated or not by this reduction. Yet, the author

(1) This Bulletin, **4** (1929), 129.
(2) *Ber.*, **35** (1902), 966.
(3) *J. Pharm. Soc. Japan*, (1918) p. 100 (in Japanese.)

feel to be justified to call this new double molecular substance "Bis-8,8'-demethoxy-dihydro-sinomenine".

II.

By the Na-amalgam reduction of dihydro-sinomenine, a monomolecular substance $C_{18}H_{23}NO_3$ was obtained in a yield about 65%. It crystallized in stout prisms from acetone. It has only one methoxyl group, retains the original keton group, and accordingly, it may be called demethoxy-dihydro-sinomenine.[1] As is seen from the following table, it is an optical antipode of Speyer's *l*-dihydrothebainone in all probability. The racemisation was carried out with the iodomethylates of the both substances.

Table 2.

	Demethoxy-dihydrosino-menine (from hydro-sinomenine)	Speyer's dihydrothebainone (from thebain)
Yield	ca. 65%	ca. 20%
M. p.	138°	151° (Speyer) 138° (Skita)
Crystall form	prisms	prisms
In alcohol	easily soluble	easily soluble
In acetone	less soluble	less soluble
Mol. wt.	385 (calc. 301)	——
$[\alpha]_D$ (free base)	+59.17°	−80.12° (Skita)
$[\alpha]_D$ (hydrochloride)	+48.88°	−50.71° (Speyer)
Methoxyl	one	——
M. p. of iodomethylate	120°	120°
M. p. of semicarbazone	235°	226° (Speyer) 237° (Goto)
$FeCl_3$-reaction	+in alcohol	+in alcohol
Diazo-reaction	+in 2,500,000th dilution	+in 2,500,00th dilution
$K_3Fe(CN)_6$-reaction	+in 500,000th dilution	+in 500,000th dilution
Formaline-SO_4H_2	+Yellow → green	yellow → green

The specific rotatory power of the free base of demethoxy-dihydro-sinomenine is somewhat lower than that given by Skita, yet that of the hydrochloride coincides fairy well with the figure given by Speyer.

As regards the melting point of the semicarbazone of Speyer's dihydro-thebainone, it is generally believed to be at 226°[2] Yet, the semicarbazone,

(1) Reduction of an ether-group, which situates vicinally to a ketone, was also obtained by Wieland and Kotake in dihydro-des-N-methyl-dihydro-codeinon, *Ann.*, **444** (1925), 69.

(2) Gulland and Robinson. *J. Chem. Soc.*, **1923**, 1006.

which the author prepared from dihydro-thebainone and recrystallized from acetone melted at 237°, thus only two degrees higher than that of demethoxy-dihydrosinomenine. The mixed melting point of these two semicarbozone was at 235°.

III.

When sinomenine is reduced with zinc-amalgam in the hot, after the method of Clemmensen, it gives a substance of the composition $C_{18}H_{25}NO_2 + \frac{1}{2}H_2O$ in a yield about 20%. It melts at 148°, contains only one methoxyl group, but no keton group. The original phenol group seems to be intact, since it gives the strong ferric chloride reaction (in alcohol), the diazoreaction and ferri-cyanide reaction in an undiminished degree. This substance, which is to be called demethoxy-desoxo-dihydrosinomenine, is evidently the d-form of the ß-tetra-hydro-desoxy-codein, as is seen from the following table. This point was proved by the actual racemisation.

Table 3.

	Demethoxy-desoxo-dihydrosinomenine	ß-Tetrahydrodesoxy-codein[1]
Yield	20%	——
M. p.	147~148°	147~148°
Cystall form	hexagonal plates	hexagonal plates
Mol. wt.	322 (calc. 287)	——
$[\alpha]_D^{19}$	+43.22°	weakly left
M. p. of iodomethylate	267°	263°
M. p. hydro-iodide	245°	240~241°
M. p. of hydrochloride	——	262
$FeCl_3$	+in alcohol	+in alcohol
Diazo-reaction	+in 2,000,000th dilution	+in 2,000,000th dilution
$K_3Fe(CN)_6$-reaction	+in 500,000th dilution	+in 500,00th dilution
Formaline-H_2SO_4	yellow → purple	yellow purple

Hydrosinomenine gives also the same substance by the Clemmensen's reduction.

(1) Frennd, *J. prakt. Chem.*, **101** (1921), 1.

IV.

If sinomenine is, as we insists, an enol-ether, it may be hydrolysed on its enol-ether group and give rise to a new ketone, as is the case with thebaine. This is actually so. When sinomenine was heated on a steam bath with 2N, 4N, 6N, 8N or fuming hydrochloric acid for two hours, and the base was set free with ammonia, then a new substance of melting point >312° was obtained in a yield about 10%. This substance contained only one methoxyl group and one ketone group against each molecule of sinomenine. But the measurement of the molecular weight showed clearly that it had a double molecular weight. We propose to call this substance "Bis-[demethyl]-sinomenyliden." The property of this substance is given in Table 4.

Table 4.

Yield	10%
M. p.	>312°
Crystall form	prisms
Mol. wt.	650 (calc. 602)
$[\alpha]_D$ (hydrochloride)	+335.52°
M. p. of iodomethylate	>300°
Methoxyls	two (one against each sinomenine molecule)
M. p. of monosemicarbazone	>300°
M. p. of dioxim	>300°
$FeCl_3$-reaction	brown (weak)
Diazo-reaction	+in 2,000,000th dilution
$FeK_3(CN)_6$-reaction	transitory
Formaline-H_2SO_4	yellow → green → bordeau

The condensation of the two molecules of demethyl-sinomenine may be interpreted in the following way. The hydrolysis of the enol-ether may cause a new ketone group to be introduced and the original double linking to be eliminated. The third nucleus of the phenanthrene takes, therefore, the aspect of diacetyl. As Pechmann[1] has proved in 1888, diacetyl or similarily constituted diketones undergo the condensation by the action of alkali, and give substituted chinones. The same condensation may occur with the demethoxylated sinomenine through ammonia. As to the positions of the condensation, we should like to assume C_6 (ketone group) and C_8

(1) *Ber.*, **21** (1888), 1417.

(methylen group) of each sinomenine molecule, thus giving a chinone like constitution to the new substance.

One uncertainty about this assumption is that this condensed substance is colourless, even in solution. Yet the fact that it forms a monoxim by the ordinary treatment with hydroxylamine hydrochloride seems to favour the chinone constitution.

V.

Throughout the preceeding sections, the author maintained the view that sinomenine must be an α, β-unsaturated ketone. If this is correct, the double linking of sinomenine must be reduced by hydrogen in status nascendi.

The reduction of sinomenine with Na-amalgam can also be cited in this favour, yet the action of Na-amalgam does not exclude the might-be catalytic action of quicksilver.

After long fruitless trials, the author succeeded at last in reducing sinomenine by zinc dust and hydrochloric acid in the cold. The yield of dihydrosinomenine was, however, scanty (=about 15% in the experiment of a small scale). The reason why such experiments did not succeed for a long time can be sought in the fact that sinomenine is less resistant against hot dilute acid. The heating sinomenine with zinc dust and acetic acid, for example, might lead invariably to the derivative of sinomenine-hydrate,[1] and not that of sinomenine.

By the way, it may be added here that sinomenine can be reduced by Clemmensen's zinc-amalgam and hydrochloric acid in the cold into dihydro-sinomenine (yield 60%). Here neither the trace of bis-8,8′-demethoxy-dihydrosinomenine nor demethoxy-desoxo-dihydrosinomenine was met with. This method may be advantageously applied to those α, β-unsaturated ketones, which by the reduction with Na-amalgam invariably undergo condensation.

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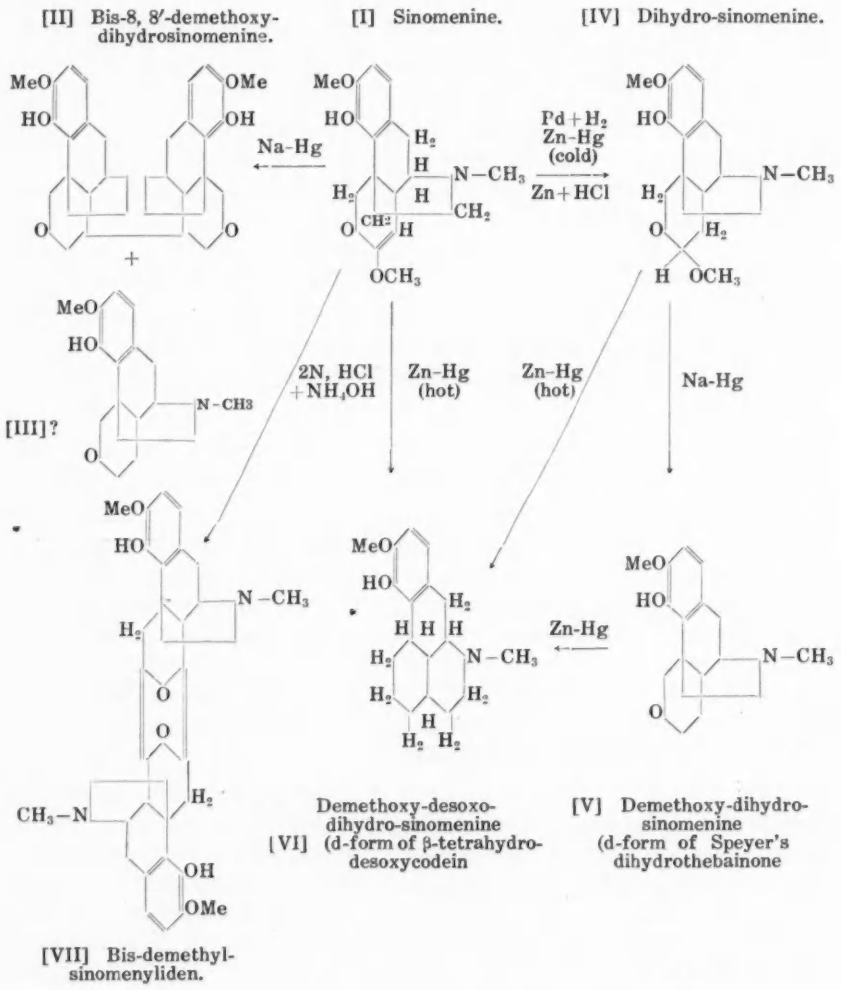
(1) Part XII of this communication, which will be published in the December number. Note.—Reduction of sinomenine with sodium resp. zinc-amalgam was carried out by Kondo and Ochiai some time ago with totally different results. Compare, *Ann.*, **470** (1929), 224.

The above described transformation of sinomenine can be summarised in the following diagram.



Experimental.

Preparation and Properties of Bis-8, 8′-demethoxy-sinomenine. Sinomenine hydrochloride (5g.) is dissolved in 2% caustic soda (50 c.c.) and added with 40gr. 3% Na-amalgam (in four portions). Within 23 hours, the apueous part is saturated with carbon dioxide. The precipitate is collected and redissolved in chloroform. The crystalline residue, which remains on the evaporation of chloroform, is once boiled with a little acetone to remove impurities und recrystallised from a large quantity of alcohol. The pure substance crystallises in stout prisms, and melts at 304°. Yield about 1.5gr. (40%).

From the soluble part remaining in carbonic acid solution, a substance, melting at 134° was isolated. This seems to be very similar to the demethoxy-dihydro-sinomenine, which will be treated later.

As to the properties of bis-8,8′-demethoxy-hydrosinomenine, see the Table 1 in the theoretical part.

Anal. Found: C=70.95, 71.10, 71.94,; H=7.70, 7.77, 7.65; N=4.56%. Calc. for $(C_{18}H_{22}NO_3)_2$=600: C=72.00; H=7.33; N=4.66%.

Methoxyls Found: 11.37, 10.77. Calc. for one: 10.26%.

Mol. wt. Found (in glacial acetic acid): 650.

Sp. rotatory power: 0.8777gr. subst. was dissolved into 25 c.c. 1% hydrochloric acid solution. l=1 dm; $\alpha=-0.86$. $[\alpha]_D^{17}=-24.49°$

Semicarbazone: M. p. >300. (Found: N=14.07%. Calc. for disemicarbazone: N=15.68%).

Methiodide: M. p. >305°, needles. (Found: I=27.45%. Calc.: I=28.72%,)

Preparation and Properties of Demethoxy-dihydrosinomenine. The condition of the reduction is almost equal with the foregoing. The free base crystallises out from acetone slowly in prisms. It softens at 125° and melts at 138°. By drying at 100° over P_2O_5 in vacuum, it becomes syrupy. Yield: 3.9gr. from 6gr. of hydrosinomenine (65%).

The elimination of the methoxyl group seems to go on rather slowly and, even when a large quantity of Na-amalgam was used, the part, which crystallises afterwards, shows a little higher methoxyl number than calculated. The properties were given in Table 2.

Anal. Found: C=71.77; H=8.11; N=4.56%. Calc. for $C_{18}H_{23}NO_3$=301: C=71.76; H=7.64; N=4.65%. Methoxyl. Found: 10.91%. Calc. for one: 10.23%.

Mol. wt. Found (in glacial acetic acid): 358.

Sp. rotatory power. 1.0097gr. Subst. were dissolved into 25 c.c. alcoholic solution. l=1 dm. $\alpha=+2.39$, $[\alpha]_D^{19}=+59.17°$. 0.9718 gr. free base was dissolved into 25 c.c. 1% hydrochloric acid solution. l=1 dm. $\alpha=+1.90$, $[\alpha]_D^{19}=+48.88°$.

Semicarbazone. Prepared in the ordinary way, and recrystallised from acetone. M. p. 235°. (Found : N=15.66%. Calc : N=15.68%).

Methiodide : prisms collected in rosetts, (from water). M. p. 115° (Found : I=26.87%. Calc. : I=28.65%).

Racemisation of Demethoxy-dihydrosinomenine Iodomethylate with Dihydrothebainone Iodomethylate. Dihydrothebainone used in this experiment was prepared by the reduction of thebaine (10gr.) with Pd-H_2 and the sorption of hydrogen amounted to over two molecules (ca. 1600 c. c.). The mixture of the reduced bases was treated with 2% caustic soda solution (150 c. c.). The alkali soluble bases (yield : 2.8gr.) was tried to racemise with demethoxy-dihydrosinomenine, but, in contrary to the expectation, the crystalls obtained in this experiment turned the polarised light slightly left. The alkali soluble base thus seemed to have been still contaminated with dihydrothebainone.(1)

The alkali soluble part was, therefore, turned into its iodomethylate and the part, which directly crystallised out from methyl alcohol, was filtered away. The filtrate was evaporated and the residue crystallised from a little water. The fine crystalls thus obtained melted at 120°, viz. at the same point with the iodomethylate of desmethoxy-dihydrosinomenine. The specific rotatory power of the two iodomethylates is given below.

Demethoxy-dihydrosinomenine iodomethylate : $[\alpha]=+36.12°$ (0.3128 gr. subst, was dissolved into 10 c. c. water. $l=10$ cm., $\alpha=1.13$).

Dihydrothebainone iodomethylate : $[\alpha]=-34.36°$ (0.3148 gr. subst. was dissolved into 10 c. c. water. $l=5$ cm., $\alpha=0.54$).

To racemise the both iodomethylates, the above solutions were evaporated to a small bulk separately and mixed together in the hot. The beautiful prisms separated out instantly while hot, which melted at 231° sharply. The remarkable exaltation of the melting point might be due to the fact that recemic iodomethylate contained no crystal water. These crystalls did not rotate the polarised light.

0.5450 gr. subst. was dissolved into 10 c. c. water. $l=10$ cm., $\alpha=\pm 0$.

Preparation and Properties of Demethoxy-desoxo-dihydrosinomenine (d-form of β-Tetrahydro-desoxy-codein). Sinomenine hydrochloride (4 gr.) was added to the Clemmensen's zinc amalgam (prepared from 14gr. $HgCl_2$+ 7~10gr. Zn), poured on with hydrochloric acid (1 : 1 ; 10 c.c.) and heated on the steam bath for 6 hours. During the heating, the hydrochloric acid of the same concentration was added in small portions from time to time (the total amount 30 c.c.). After standing overnight, 25 c.c. of the filtrate

(1) Skita, *Ber.*, **54** (1921), 1561. This is presumably the iodomethylate of dihydrothebaine.

were obtained, from which separated a syrupy precipitate when added with the same amount of water. The precipitate was dissolved in acetone (10 c.c.) and poured into chloroform (100 c. c.). The chloroform was washed thoroughly with ammonia to decompose the zinc double salts. The dried chloroform was evaporated and a little acetone was added to the residue. On cooling it with tap-water, the substance crystallised out in prisms. The yield was scanty (0.1gr. from the above treatment and 0.1gr. from the not precipitated part). M.p. 148°. With hydrosinomenine, the yield was somewhat better (30%).

The properties of this substance were given in Table 3. The big hexagonal plates (as were described by Freund) are obtainable when recrystallised from a large quantity of hot acetone.

Anal. Found: C=73.10, 73.42; H=8.38, 8.33; N=4.53. Calc. for $C_{18}H_{25}NO_2\frac{1}{2}H_2O$= 296: C=72.97; H=8.73; N=4.72%.

Methoxyl. Found: 10.15, 10.16%. Calc. for one: 10.47%.

Mol. wt. Found (in glacial acetic acid): 322. Calc.: 296.

Sp. rotatory power. 0.7982gr. substance was dissolved into 25 c.c. alcoholic solution. l=1 dm., α=+1.38. $[\alpha]_D$=+43.22°.

Methiodide: M. p. 267° (long needles from alcohol). Found: I=28.30 Calc.: I=29.59%.

Hydro-iodide, (prepared after Freund)(1): Long needles, m. p. 245°.

The substance does not make a semicarbazone.

Racemisation of Demethoxy-desoxo-dihydrosinomenine with β-Tetrahydrodesoxy-codeine. The β-tetradesoxy-codeine used in this experiment was prepared from codeine by the method of M. Freund.(1) It melted at 148°. As regards the colour reactions, see the right-hand column of Table 3.

For the racemisation, ca. 0.5 gr. of each substance was mixed in acetone solution. The crystalls (ca. 0.7gr.), which separated out instantly on cooling, were collected and redissolved in hot acetone. When acetone was evaporated down to ca. 6 c.c. in a cool place, ca. 0.3gr. substance was deposited in beautiful crystals. This was collected and examined on its rotatory power.

0.2949 gr. substance was dissolved into 10 c.c. chloroform. l=10 dm., $\alpha = \pm 0$.

The racemisation was thus complete. The racemic substance melted at 135° (from acetone). The iodomethylate prepared therefrom melted at 232° (from water).

Preparation and Properties of Bis-(demethyl)-sinomenyliden. Sinomenine hydrochloride (10gr.) is dissolved in 100 c.c. 2N hydrochloric acid, and heated on the steam bath for 2 hours. The base is set free with

(1) *J. prakt. Chem.*, **101** (1921), 30.

ammonia and extracted with chloroform. The substance is easily crystalliable. M.p. >312°. Yield ca. 10%.[1]

For the properties of bis-[demethyl]-sinomenylinen. see Table 4.

Anal. Found : C=71.90, 71.43 ; H=6.95, 6.86 ; N=5.04%. Calc. for $(C_{18}H_{21}NO_3)_2$=598 : C=72.24 ; H=7.02 ; N=4.68%.

Methoxyls. Found : C=10.07, 10.08%. Calc. for two (one for each sinomenine molecule) 10.36%.

Mol. wt. Found (in glacial acetic acid) : 622.

Sp. rotatory power. 0.9694 gr. substance was dissolved into 25 c.c. 1% hydrochloric acid. l=1 dm., α=+13.01, $[\alpha]_D^{17}$=+335.52

Methiodide : Very fine needles from water. M.p. 285° (?). Found : I=27.2% Calc. : I=28.78%.

Dioxim : M.p. >315° from chloroform. Found : N=8.66% Calc. for dioxim : N=8.91%.

Semicarbazone : M.p. >300°, prepared in the oridinary way. Found : N=7.29%. Calc. for disemicarbazone : N=14.96%.

Reduction of Sinomenine with Nascent Hydrogen. Sinomenine hydrochloride (1gr.) was dissolved in 30 c.c. 4% hydrochloric acid and added with 5gr. granular zinc. The mixture is cooled with water, and added with 10% hydrochloric acid from time to time (50 c.c. in total). Extracted in ordinary way and recrystallised from methyl alcohol, the reaction mixture gave 0.15gr. hydrosinomenine (m.p. 196° ; mixed melting point with that obtained by palladium-hydrogen reduction was 197°).

The mixture of sinomenine hydrochloride (4.5 gr.) zinc amalgam (ca. 10 gr.) and hydrochloric acid (1 : 1, ca 50 c.c.) was left overnight in a cool place. The filtrate gave no precipitate on the addition of water, but about 2.4 gr. hydro-sinomenine were isolated from it (m. p. 192°).

Hydrosinomenine, morphine and codein were not reduced in the above treatment. The reduction mixture of codeinone gave much precipitate with water, but it was not further studied.

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(1) A better yield will be achieved when sinomenine hydrate is decompcsed by ammonia (see Part XII).

SOME NOTES ON THE THEORY OF ELECTRO-OSMOSIS. PART I.

By Sakuji KOMAGATA.

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1. Introduction. The phenomenon of electro-osmosis was, at first, discovered by Reuss, Russian scientist, on 1808. Since then, many authorities have been in research on this subject. The phenomenon takes place in the following familiar experiment: the bath is separated by a membrane (for examples, porcelain, texture and glass powder etc.) as shown in Fig. 1. The electrodes are inserted in each chamber and the electromotive-force is applied between them. Then, the liquid flows out through capillaries of membrane under the applied electric force, the level of one chamber being raised up over that of the other.

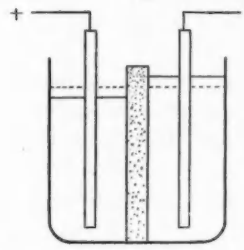

Fig. 1.

The mechanism for this phenomenon is considered to be due to the electric double layers existed on the surface of capillary wall. This theory was chiefly treated by Helmholtz, Lamb, Smoluchowski and others, and the very simplified following equation was dedused:

$$W=\frac{\zeta VDA}{4\pi\mu L}\ , \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (1)$$

where W is the quantity of liquid flowed out per unit time; A, the area of capillary; L, the length of capillary; ζ, the potential of double layers; V, the applied electric field; D, the dielectric constant of liquid; μ, the coefficient of viscosity of liquid.

But, we can also treat the theory of electro-osmosis in far more details under some assumptions. The purpose of this paper is to present one of these methodes carried out, as follows.

2. Electrical Condition in Capillary. Generally, at the surface of separation of two different materials, the ionic balance differs from that in the inner part of them. One kind of ion, positive or negative, accumulates there over the another kind of ion, according to the electrical properties of these materials.

The electrical condition in capillary is an interesting problem on the physical point of view. In our problem, the variation in configuration of electric charges takes place only in the capillary, because the solution in capillary are far more ionized than the materials of capillary wall.

For the convenience to the mathematical treatment, here we use the cylindrical coordinates (r, θ, z), z-axis being coincided with the axis of capillary as shown in Fig. 2. To neglect the effect of its terminals, the capillary is of infinite length for both directions of z.

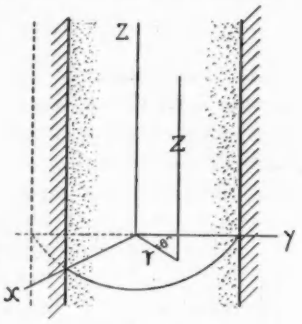

Fig. 2.

Let φ, be the potential;
ρ, the electric charge;
T, the absolute temperature;
C, the concentration;
D, the dielectric constant of liquid;
R, the radius of capillary;
k, Boltzmann's constant;
F, Faraday's constant.

The following two relations are established in this case:

(a) Equation of Poisson.

$$\Delta\varphi = -\frac{4\pi}{D}\rho \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (2)$$

(b) Maxwell-Baltzmann's distribution law. For the sake of simplicity, we take up the special case of monovalent ion as follows. That is,

$$\rho = F(C_+ - C_-) \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

$$= FC_0\left(e^{-\frac{\varphi F}{kT}} - e^{\frac{\varphi F}{kT}}\right)$$

$$= -FC_0 \sinh\frac{\varphi F}{kT} \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (4)$$

where C_0 is the concentration for $\varphi = 0$.

For the small quantity of $\left(\frac{\varphi F}{kT}\right)$, we can neglect the higher power of $\left(\frac{\varphi F}{kT}\right)$ and obtain the simplified equation:

$$\rho = \frac{2C_0F^2}{kT}\varphi \ , \quad \cdots\cdots\cdots\cdots\cdots\cdots \quad (5)$$

From (2) and (5),

$$\Delta\varphi=\frac{\partial^2\varphi}{\partial r^2}+\frac{1}{r}\frac{\partial\varphi}{\partial r}=\frac{8\pi F^2C_0}{DkT}\varphi=\varkappa^2\varphi\ , \quad \ldots\ldots\ldots\ (6)$$

where $$\varkappa=\sqrt{\frac{8\pi F^2C_0}{kDT}}\ , \text{ say } \ldots\ldots\ldots\ldots\ldots\ (7)$$

Also from (5) and (7),

$$\rho=\frac{D}{4\pi}\varkappa^2\varphi \ . \quad \ldots\ldots\ldots\ldots\ldots\ (8)$$

The solution of (6) is given by;

$$\varphi=C_1J_0(i\varkappa r)+C_2Y_0(i\varkappa r)\ , \quad \ldots\ldots\ldots\ (9)$$

where C_1 and C_2 are the integration constants to be determined from the boundary conditions; J_0 and Y_0 are Bessel functions of zeroth order of first and second kind respectively.

For $r=0$, φ does not become infinite. That is, $C_2=0$.

At the surface of separation (capillary wall) $r=R$, we have

$$\varphi=\varphi_0\ , \quad \ldots\ldots\ldots\ldots\ldots\ (10)$$

and

$$\frac{\partial\varphi}{\partial r}=-\frac{4\pi}{D}\eta_0\ , \quad \ldots\ldots\ldots\ (11)$$

where η_0 is the surface density of charge at the separation.

From (10), $$C_1=\frac{\varphi_0}{J_0(i\varkappa R)} \ . \quad \ldots\ldots\ldots\ (12)$$

or, from (11), $$\left[\frac{\partial\varphi}{\partial r}\right]_{r=R}=-C_1i\varkappa J_1(i\varkappa R)=-\frac{4\pi}{D}\eta_0\ ,$$

$$C_1=\frac{4\pi N_0}{Di\varkappa J_1(i\varkappa R)} \ . \quad \ldots\ldots\ldots\ (13)$$

But, from equation (8), the total charge in capillary per unit length is given by

$$2\pi\int_0^R\rho.r\,dr=2\pi\frac{D}{4\pi}\varkappa^2C_1\int_0^R rJ_0(i\varkappa r)dr$$

$$= -\frac{2\pi R D i\varkappa J_1(i\varkappa R) C_1}{4\pi}$$

$$= -2\pi R\eta_0 \ , \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (14)$$

This is, the total charge in capillary is equal to the total surface charge at the surface of capillary wall in amount but with opposite sign. This is the condition which satisfies our problems.

The distribution of potential is:

$$\varphi = \varphi_0 \frac{J_0(i\varkappa r)}{J_0(i\varkappa R)} \quad \text{[from (12),]} \quad \ldots\ldots\ldots\ldots \quad (15)$$

$$= \frac{4\pi\eta_0 J_0(i\kappa r)}{D i\varkappa J_1(i\varkappa R)} \quad \text{[from (13),]} \quad \ldots\ldots\ldots\ldots \quad (16)$$

and
$$\left.\begin{aligned} [\varphi]_{r=o} = \varphi^* &= \frac{\varphi_0}{J_0(i\varkappa R)} \\ &= \frac{4\pi\eta_0}{D i\varkappa J_1(i\varkappa R)} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (17)$$

and
$$[\varphi]_{r=R} = \varphi_0 = \frac{4\pi\eta_0 J_0(i\varkappa r)}{D i\varkappa J_1(i\varkappa R)} \quad \ldots\ldots\ldots\ldots\ldots \quad (18)$$

The distribution of charge is:

$$\rho = \frac{D\varkappa^2\varphi_0 J_0(i\varkappa r)}{4\pi J_0(i\varkappa R)} \quad \text{[from (12),]} \quad \ldots\ldots\ldots\ldots \quad (19)$$

$$= \frac{\varkappa\eta_0 J_0(i\varkappa r)}{i J_1(i\varkappa R)} \quad \text{[from (13),]} \quad \ldots\ldots\ldots\ldots \quad (20)$$

and
$$\left.\begin{aligned} [\rho]_{r=o} = \rho^* &= \frac{D\varkappa^2\varphi_0}{4\pi J_0(i\varkappa R)} \\ &= \frac{\varkappa\eta_0}{i J_1(i\varkappa R)} \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (21)$$

and
$$[\rho]_{r=R} = \frac{D\varkappa^2\varphi_0}{4\pi} = \frac{\varkappa\eta_0 J_0(i\varkappa R)}{i J_1(i\varkappa R)} \quad \ldots\ldots\ldots\ldots \quad (22)$$

The distribution of charges is shown in Fig. 3.

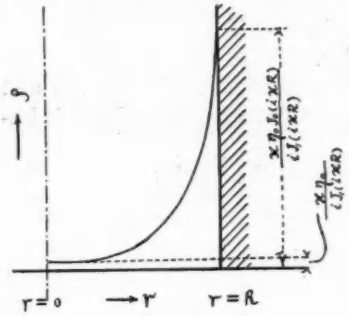

Fig. 3.

From the fact mentioned in (14), we can replace this configuration by the effective condenser. This is the so-called condenser-like-configuration of electrical double layers. Let a and b the radii of inner and outer concentric cylinders respectively, then the capacity per unit length is given by $\frac{D}{2\log\left(\frac{b}{a}\right)}$. Therefore, putting δ the distance between two concentric cylinders, we have

$$\frac{D}{2\log\left(\frac{b}{a}\right)}=\frac{D}{2\log\frac{R}{R-\delta}}=q \text{ , say } \ldots\ldots\ldots \quad (24)$$

Therefore, we have $$\delta=R\left(1-e^{-\frac{D}{2q}}\right) , \ldots\ldots\ldots\ldots\ldots\ldots \quad (25)$$

where $$q=\frac{2\pi\int\rho r dr}{\varphi_0-\varphi^*}=\frac{RD\varkappa\{-iJ_1(i\varkappa R)\}}{2\{J_0(i\varkappa R)-1\}} \ldots\ldots\ldots \quad (26)$$

Actually, in some cases, one part of ions in capillary are adsorbed on the capillary wall by the specific adsorption, as shown in Fig. 4. Then the distributions of potential and charge are far more complicate than that discussed above.[1] But, here we will not enter into these subjects further.

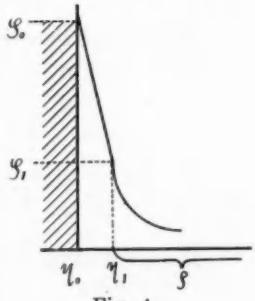

Fig. 4.

And, for the mixture of polivalent ions, the equations become complicate, but the just similar considerations are also to be carried out.

3. Electro-osmotic Flow in Capillary. Let us consider the steady motion of liquid through capillary under applied electric force.

Let us take the coordinates the same used in Section 2, and also

v, be the velocity of flow;

p, the pressure;

(1) Cf. O. Stern, *Z. Elektrochem.*, **30** (1923), 508.

d, the density;
μ, the coefficient of viscosity;
ν, the kinematic coefficient of viscosity ($=\mu/d$);
E, the applied electric field intensity.

For a considerable small capillary, it is questionable whether μ, ν and D are given by their normal values or not. Although this problem is important, it is not yet been made clear now.

The lines of flow in this case are all parallel to the z-axis:

$$v_x=v_y=0 \ .$$

As the liquid is considered to be imcompressible, we have also

$$\frac{\partial v_z}{\partial z}=\frac{\partial v}{\partial z}=0 ,$$

that is, v is the function of x and y, but not of z.

The electric charges are set in motion under the applied electric force toward the electrode of opposite sign. And the liquid element is, too, acted by the force due to the resultant volume charges which are contained in it. Here, we assume that the distribution of charges in this case is the same as that discussed in section 2 and that the body force acting on the liquid element is equal to that on the resultant volume charges in it. Then, the body force is given by:

$$K=EF(C_+-C_-)=\rho E=\rho^* J_0(ix r)E=K_0 J_0(ix r) \ , \quad \ldots\ldots \quad (27)$$

where

$$K_0=E\rho^*=\frac{xE\eta_0}{iJ_1(ixR)} \ . \quad \ldots\ldots\ldots\ldots\ldots \quad (28)$$

Resulting from these considerations, the following equation of hydrodynamics for viscous liquid is applicable:

$$K-\frac{1}{d}\ \mathrm{grad}\ p+\nu\Delta v=0 \ , \quad \ldots\ldots\ldots\ldots\ldots \quad (29)$$

or

$$K_0 J_0(ix r)-\frac{1}{d}\frac{\partial p}{\partial z}+\nu\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial v}{\partial r}\right)=0 \ . \quad \ldots \quad (30)$$

Differentiating (30) with z, we have

$$\frac{\partial^2 p}{\partial z^2}=0 ,$$

therefore

$$\frac{\partial p}{\partial z}=a \ . \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (31)$$

where a is the integration constant.

Inserting (31) into (30) and integrating with r twice, then we have

$$v=\frac{a}{4\mu}r^2-\frac{K_0}{\varkappa^2\nu}J_0(i\varkappa r)+A\log r+B \quad \ldots\ldots\ldots \quad (32)$$

where A and B are the integration constants. The boundary conditions are:

(i) v is not infinite at $r=0$; $A=0$. (33)

(ii) The liquid is not in motion on the surface of capillary wall;

$$[v]_{r=R}=0 \ .$$

So
$$B=\frac{K_0 J_0(i\varkappa R)}{\varkappa^2\nu}-\frac{a}{4\mu}R^2 \quad \ldots\ldots\ldots\ldots \quad (34)$$

Therefore,
$$v=\frac{1}{4}\frac{a}{\mu}(r^2-R^2)+\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)] \quad \ldots\ldots \quad (35)$$

Now, let the length of capillary be L ($L \gg R$) and the pressures at two ends be p_1 and p_2 respectively, then

$$\frac{\partial p}{\partial z}=a=-\frac{(p_1-p_2)}{L} \quad \ldots\ldots\ldots\ldots\ldots \quad (36)$$

So
$$v=\frac{(p_1-p_2)}{4\mu L}(R^2-r^2)+\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)] \quad \ldots\ldots \quad (37)$$

If the pressure difference between two ends of capillary be very small compared with the body force acting on the liquid, then we can neglect the first term in (37):

$$v'=\frac{K_0}{\nu\varkappa^2}[J_0(i\varkappa R)-J_0(i\varkappa r)] \ , \quad \ldots\ldots \quad (38)$$

which is shown in Fig. 5.

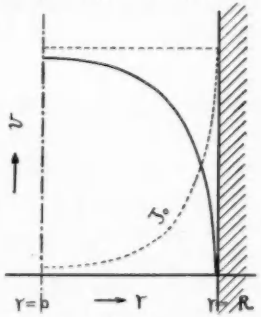

Fig. 5.

The quantity of liquid flowed out through capillary per unit time is

$$W=2\pi\int_0^R vr\,dr$$

$$=\frac{\pi(p_1-p_2)}{8\mu L}R^4+\frac{2\pi K_0}{\nu\varkappa^2}\left[\frac{R^2}{2}J_0(i\varkappa R)+\frac{iRJ_1(i\varkappa R)}{\varkappa}\right] \quad \ldots \quad (39)$$

Also, if we neglect the first term, we obtain

$$W' = \frac{\pi R^2 K_0}{\nu\varkappa^2}\left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R}\right] . \quad \cdots\cdots\cdots \quad (40)$$

If we can balance the hydrostatic force and the electric force,

$$W = 0 ,$$

or

$$\frac{p_1 - p_2}{L} = \frac{P}{L} = -\frac{8\mu K_0}{\nu\varkappa^2 R^2}\left[J_0(i\varkappa R) + \frac{2iJ_1(i\varkappa R)}{\varkappa R}\right] . \quad \cdots\cdots \quad (41)$$

The electric charges are transfered by the flow of liquid. This amount per unit time is given by the equation:

$$\begin{aligned} Q &= 2\pi\int_0^R \rho v r\, dr \\ &= 2\pi\int_0^R r\rho^* J_0(i\varkappa r)\left[\frac{a}{4\mu}(r^2 - R^2) + \frac{K_0}{\nu\varkappa^2}\Big(J_0(i\varkappa R) - J_0(i\varkappa r)\Big)\right] dr \\ &= \frac{\pi\rho^* a R^2}{\mu\varkappa^2} J_2(i\varkappa R) + \frac{\pi\rho^* K_0 R^2}{\nu\varkappa^4}\left\{\left[J_0 i\varkappa R\right]^2 - 2\left(\frac{\varkappa}{R}\right)\Big[J_0(i\varkappa R) J_1(i\varkappa R)\Big]\right. \\ &\qquad \left. + \Big[J_1(i\varkappa R)\Big]^2\right\} . \quad \cdots\cdots\cdots\cdots\cdots \quad (42) \end{aligned}$$

When $a = 0$, the first term in (42) vanishes as in the equation (38) and (40).

4. Electric Current through Capillary. In the present section, we consider the electric current through capillary. From Section 2, we can obtain the values of the charges:

$$\rho_+ = FC_0 e^{-\frac{\varphi F}{kT}} . \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (43)$$

$$\therefore FC_0\left\{1 - \frac{\varphi F}{kT}\right\} = FC_0\left\{1 - \frac{\rho^*}{2FC_0} J_0(i\varkappa r)\right\} . \quad \cdots\cdots \quad (44)$$

$$\rho_- = FC_0 e^{-\frac{\varphi F}{kT}} . \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (45)$$

$$\therefore FC_0\left\{1 + \frac{\varphi F}{kT}\right\} = FC_0\left\{1 + \frac{\rho^*}{2FC_0} J_0(i\varkappa r)\right\} . \quad \cdots\cdots \quad (46)$$

The electric current (I) required is given by the equation:

$$i = E(\rho_+ m_+ + \rho_- m_-) , \quad \cdots\cdots\cdots\cdots\cdots \quad (47)$$

and $$I=2\pi\int_0^R ir\,dr \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (48)$$

where m_+ and m_- are the mobilities of ions. The electro-osmotic flow takes place in capillary as has treated in Section 3. For example, let the electro-osmotic flow be directed from the positive electrode to the negative, then, the negative charges are prevented their motion by the flow, and contrary to it, the positive charges are promoted their motion. Therefore, the mobility is smaller for negative ions and greater for positive ones than the normal values, and moreover differs from place to place as velosity does. But, as far as this flow is very small, this deviation is also small. In general, the mobility will be smaller in such a small capillary than in a normal free state.

But assuming here m_+ and m_- to be their normal values, then we have from (44), (46), (47) and (48),

$$i=EFC_0\left[\left\{1-\left(\frac{\rho^*}{2FC_0}\right)J_0(ixr)\right\}m_+ + \left\{1+\left(\frac{\rho^*}{2FC_0}\right)J_0(ixr)\right\}m_-\right]. \quad (49)$$

and

$$I=2\pi EFC_0\int_0^R\left[(m_+ + m_-)r-(m_+ - m_-)\left(\frac{\rho^*}{2FC_0}\right)rJ_0(ixr)\right]dr$$

$$=EFC_0\pi R^2(m_+ + m_-)\left\{1+\left(\frac{m_+ - m_-}{m_+ + m_-}\right)\left(\frac{\rho^*}{2FC_0}\right)\left(\frac{iJ_1(ixR)}{xR}\right)\right\}. \quad (50)$$

The first term, $EFC_0\pi R^2\,(m_+ + m_-)$, is the current established in the large vessel. Therefore, the current differs in the capillary by the amount equal to the second term.

Summary

(1) Under some assumptions, the distributions of potential and electric charge in capillary are given by the equations (15)—(22) . . . . (Section 2.)

(2) The quantity of liquid flowed out electro-osmotically W' is given by the equation (40), and $W'/\pi R^2$ is expressed by the function of radius R. The relation between permeability of membrane and electro-osmotic transfer has already been pointed out[1] to be different from that given by the Helmholtz's equation in which $W'/\pi R^2$ is constant for any R, although it is only considered to be caused from the "free-osmosis"—that is, equivalent to the first term in right hand member of equation (39). . . . . (Section 3.)

(1) A. Strickler and J. H. Mathews, *J. Am. Chem. Soc.*, **44** (1922), 1647.

(3) The current in capillary differs from that in the large vessel, because of its non-uniform distribution of electric charge. This is given by the equation (50). And, the relation between so-called surface conduction and ζ-potential seems to be slight, as D.R. Briggs[1] has stated. (Section 4.)

The writer wishes to express his hearty thanks to Prof. Setoh for his kind advice.

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STUDIES ON MERCAPTALS OF SUGARS. III. ISO-BUTYL MERCAPTALS OF SUGARS.[2]

By Yoshisuke UYEDA.

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Normal butyl[3] and normal propyl mercaptals[4] of sugars have been studied by the present author and were reported in this journal.

This paper is the outline of the results of the studies of iso-butyl mercaptals of various sugars.

Experimental.—Mercaptals are prepared by the same method as described in the previous paper.[3] The condensation is carried out by using conc. HCl (sp. gr. 1.20), as proposed by Fischer.[5] The crude products are purified by the crystallization from dilute alcohol. The new mercaptals of sugars obtained have the following chemical constitution, which are determined by the analysis; here R representing

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad CH.\ CH_2.\ S. \\ \diagup \\ CH_3 \end{matrix}$$

(1) D. R. Briggs, "Colloid Symposium Monograph", **4** (1928), 41.
(2) Read before the annual meeting of the Chemical Society of Japan, April 7, 1929.
(3) This Bulletin, **1** (1926), 179.
(4) This Bulletin, **1** (1926), 181.
(5) Fischer, *Ber.*, **27** (1894), 673.

Table 1.

		Sulphur(1)	
		Calc. %	Found %
Glucose-iso-butyl mercaptal	$C_6H_{12}O_5$ $(R)_2$	18.71	18.44
Galactose ,,	$C_6H_{12}O_5$ $(R)_2$	18.71	18.67
Mannose ,,	$C_6H_{12}O_5$ $(R)_2$	18.71	18.50
Rhamnose ,,	$CH_3 . C_5H_9O_4$ $(R)_2$	19.63	19.08
Arabinose ,,	$C_5H_{10}O_4$ $(R)_2$	20.51	20.34
Maltose ,,	$C_{12}H_{22}O_9$ $(R)_4$	19.21	19.20
Sucrose ,,	$C_{12}H_{22}O_9$ $(R)_4$	19.21	19.13

The physical constants of these mercaptals are shown in the following table.

Table 2.

	M. p.	Sp. rotation
Glucose-iso-butyl mercaptal	130°	$[\alpha]_D^{14°} = +40.0$
Galactose ,,	129°	$[\alpha]_D^{13°} = +41.2$
Mannose ,,	111°	,, $= +16.4$
Rhamnose ,,	112°	,, $= +14.0$
Arabinose ,,	123°	$[\alpha]_D^{14°} = +20.0$
Maltose ,,	140°	$[\alpha]_D^{12°} = +13.2$
Sucrose ,,	138°	$[\alpha]_D^{14°} = +9.6$

Summary.—Iso-butyl mercaptals of three hexoses, one methyl pentose, one pentose and two dioses are crystallized out as new compounds.

Other sugars, e. g. lactose, fructose, xylose are tried but ended in negative results.

The author is much indebted to Mr. Masao Hiraoka for his kind assistance.

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(1) The sulphur is determined by using Parr bomb.

REDUCTION OF TRIMETHYL STANNYL HYDROXIDE IN LIQUID AMMONIA.

By Taichi HARADA.

Received October 19, 1929. Published November 28, 1929.

The alkali metals are very strong reducing agents. Fittig and Wurtz have applied this principle in the synthesis of various hydrocarbons at ordinary temperatures in ethereal solutions; however, the rate of reaction is very slow, It has been recognized that the alkali metals, such as sodium and potassium, in liquid ammonia solution react as strong and convenient reducing agents for various organic compounds and possess the advantage that the reduction may be carried out at as low a temperature as 33.5° C. Therefore, in such a solution, the stability of the resulting substance is relatively great. The reactions involved are in many cases instanteneous and quantitative.

Metallic sodium is extremely soluble in liquid ammonia in which the following reactions probably take place:[1]

$$Na + NH_3 \rightleftarrows [NaNH_3^+ + e^-] \rightleftarrows Na + e^- + NH_3$$

$$\downarrow$$

$$NaNH_2 + H^+ + e^- \rightarrow NaNH_2 + \tfrac{1}{2}H_2$$

It is interesting to note that the characteristic blue color reaction is present even with a minute trace of sodium in the solution. In the above reaction, the formation of $NaNH_2$ and H_2 is very slow in comparison with others.

The reactions of alkali metals on organic compounds in liquid ammonia were first investigated by Moissan.[2] Since then it has been extensively developed by Lebeau[3], Lebeau and Picon[4], Kraus[5], Kraus and his students[6],

(1) Kraus *J. Am. Chem. Soc.*, **30** (1908), 1323.

(2) *Compt. rend.*, **127** (1898), 911; **136**, (1903), 1217.

(3) Lebeau, ibid., **140** (1905), 1042, 1264.

(4) Lebeau and Picon, ibid., **157** (1913), 137,223; **158** (1914), 1514; **159** (1914), 70; **173** (1921), 84; Picon, ibid., **175** (1922), 1213; Picon, *Bull. soc. chim.*, **35** (1924), 979.

(5) Kraus, *J. Am. Chem. Soc.*, **35** (1913), 1732.

(6) Kraus and Greer, *J. Am. Chem. Soc.*, **44** (1922), 2629; Kraus and White, ibid., **45** (1923), 768; Kraus and Kawamura, ibid., **45** (1923), 2756; Kraus and Sessions, ibid., **47** (1925), 2361; Kraus and Bullard, ibid., **48** (1926), 2131; Kraus and Rosen, ibid., **47** (1925), 2739; Kraus and Foster, ibid., **49** (1927), 457; Kraus and Neal, ibid., **51** (1929), 2403.

Chablay[1], Dains, Vaughan and Janney[2], Clifford[3], White[4], and White and his students[5]. Other workers will be found elsewhere. X denotes an electro-negative radical or element and R an electro-positive radical or element. Since various salts, acids and bases assume a state of more or less electrical dissociation in liquid ammonia (a condition which does not necessarily require the actual solution of these materials), they may be represented according to the following general equation :

$$R\,X \rightleftharpoons R^{+} + X^{-}$$

The reactions between organic compounds and alkali metals in liquid ammonia are extremely varied and quite complex. This is shown by Professors Kraus and White, and with their students, on a large number of experiments with various organic compounds. It has been stated that organic compounds containing strong electro-negative radicals or elements are, in general, reduced to the radical or elements of the radical, forming salts with the reducing metals, depending upon the nature of the radical in question and various other substances present. For instance, an alkyl or aryl radical is relatively strongly electro-positive and weakly electro-negative and univalent. Since the sodium salt of these groups is very unstable in liquid ammonia, it hydrolyzes (ammonolyzes) to form its hydrocarbon and amines[6]. In such an electro-negative radical, the electron is relatively loosely attached to the radical and therefore tends to combine with a more strongly electro-negative radical or element; while in the case of $(C_6H_5)_3CK$[7] or $(CH_3)_3SnNa$[8] the electron is relatively strongly or moderately strongly attached to the radical since they are not ammonolyzed in liquid ammonia solution. However the latter hydrolyzes in the presence of ammonium chloride to form trimethyl stannane, $(CH_3)_3SnH$[9].

The general reactions may be represented as follows :

$$\text{I} \qquad R^{+} + X^{-} + Na^{+} + e^{-} \rightleftharpoons R + Na^{+}X^{-}$$

$$\text{II} \qquad R^{+} + X^{-} + 2Na^{+} + 2e^{-} \rightleftharpoons R^{-}Na^{+} + Na^{+}X^{-}$$

(1) *Compt. rend.*, **140** (1905), 1262; **154** (1912), 364; **156** (1913), 1020; *Ann. Chim.*, **9.** I, (1914), 469.

(2) *J. Am. Chem. Soc.*, **40** (1918), 936.

(3) ibid., **41** (1919), 1051.

(4) ibid., **45** (1923), 779.

(5) White and Knight, ibid., **45** (1923), 1781; White, Morrison and Anderson, ibid., **46** (1924), 961; Wooster, **50,** (1928), 1388.

(6) White, *J. Am. Chem. Soc.*, **45** (1923), 779.

(7) Kraus and Rosen, *J. Am. Chem. Soc.*, **47** (1925), 2739.

(8) Kraus and Sessions, ibid., **47** (1925), 2361.

(9) Kraus and Greer, ibid., **44** (1922), 2629.

A couple of years ago, the author prepared trimethyl stannyl free radical[1] by the reduction of trimethyl stannyl hydroxide as one of the materials for the preparation or the reduction products of the so-called "Metallo Organic Oxonium Salt," $[(CH_3)_3\,Sn]_2\,O(CH_3)_3\,SnX$, with metallic sodium in liquid ammonia. The present paper will describe its method of preparation in some detail.

Apparatus. The reaction tube A is immersed in a Dewer tube B containing commercial liquid ammonia as shown in the accompanying figure.

Dewer tube B has a capacity of about 700 c.c. It is 45 cm. long, and 5.5 cm. in diameter. Ammonia dried by sodium is introduced into the reaction tube through the inlet tube C. The side tube D permits the introduction of air, oxygen or nitrogen gas, at will. The reaction tube is connected through the pinchcock F with the mercury manometer H, in which the pressure can be varied at G, as desired. The reaction tube also has a side tube J, with rubber stopper K, through which small pieces of alkali metal can be introduced into the reaction tube. The tube L with stop cock M is connected with the side tube E of the reaction tube, and by this means, ammonia and other accompanying gases can be drawn out from the manometer outlet and can be collected over the water in the burette W which is filled with water from the vessel P by suction through the stop cock O.

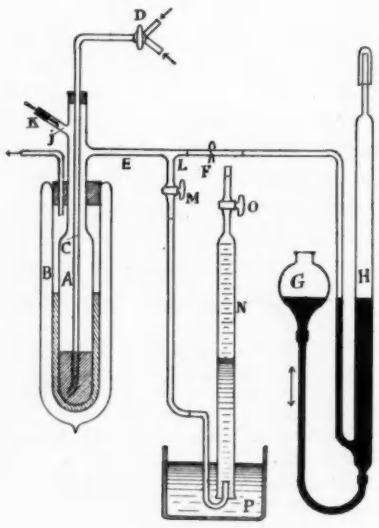

Fig. 1.

Preparation of Trimethyl Stannyl Iodide. Trimethyltin iodide was prepared by treating sodium-tin or sodium-tin-zinc alloy with methyl iodide.[2]

The alloys were treated over night with methyl iodide at room temperature and then heated on a water bath and finally in an oil bath at 120°C. The products then were separated by means of fractional distillation.

(1) This Bulletin, **2** (1927), 107.
(2) Tetramethyl tin by Cahours, *Ann.*, **111** (1859), 236 and Ladenburg, *Ann. Suppl.*, **8** (1870), 74.

Zn%	Na%	Sn%	Alloy	CH_3I	$(CH_3)_3SnI$	$(CH_3)_4Sn$
2	14	C.P. 84	128	97	trace	22.8
-	7	C.P. 93	45	35	5	-
0.5	7	Comm. 92.5	115	90	41	2
-	14	Comm. 86	92	70	trace	16

The results indicate that the amount of sodium in the alloy is a controlling factor in regard to the production of $(CH_3)_3SnI$ or $(CH_3)_4Sn$, whereas zinc is more in the nature of a catalyzer of the reaction. This material also may be obtained by treating tetramethyl tin with iodine in a bath of ice water according to the following reaction equation:

$$(CH_3)_4Sn + I_2 \longrightarrow (CH_3)_3SnI + CH_3I$$

Trimethyl Stannyl Hydroxide. This compound was prepared by treating trimethyltin iodide with concentrated sodium hydroxide in alcoholic solution and distilled.

$$(CH_3)_3SnI + NaOH \longrightarrow (CH_3)_3SnOH + NaI$$

When the alcoholic solution is evaporated under suitable conditions it gives colorless crystals. On heating, it sublimes in a white, snow-like form. It can be recrystallized out from strong alcoholic solution as large colorless crystals. It melts and sublimes at 118°C.

Trimethyl Stannyl free Radical. One molecular proportion of trimethyltin hydroxide was dissolved in liquid ammonia by passing a stream of ammonia through the clear solution and then one atomic proportion of small pieces of sodium was added slowly. Sodium reacted readily with the hydroxide without an evolution of gas along with the addition of sodium, and a white precipitate was formed and settled in the bottom of the reaction tube. When the total amount of sodium had been added to the solution, the ammonia was evaporated at room temperature and the resulting product was treated with alcohol and washed with an excess of water until free from sodium hydroxide. The yield was quantitative. The trimethyltin free radical thus obtained may be separated as a heavy, oily liquid by a separatory funnel through filter paper with anhydrous sodium sulphate in an atmosphere of nitrogen. It melts at 23°C. and boils at 181°C. and is not appreciably soluble in water.

Anal. Subst.=0.5241gr.; SnO_2=0.4840gr. Found: Sn=72.60%. Calc. for $(CH_3)_3Sn$: Sn=72.46%.

The compound was entirely identical with which obtained from trimethyltin halide with sodium in liquid ammonia by Kraus and Sessions[1].

(1) Kraus and Sessions, *J. Am. Chem. Soc.*, **47** (1925), 2361.

The free radical possesses strong reducing power. It reduces silver nitrate in solution into metallic silver instantly.

$$(CH_3)_3Sn + Ag^+ + NO_3^- \rightleftharpoons Ag + (CH_3)_3Sn^+NO_3^-$$

Kraus and Sessions show the molecular weight of the radical in benzene at boiling point, at lower concentration, to be monomolecular; and at higher concentration to be dimolecular in form. However even at low concentration at its freezing point it is completely polymerized to the stannoethane[1]:

$$2(CH_3)_3Sn \overset{\text{benzene}}{\rightleftharpoons} [(CH_3)_3Sn]_2$$

when trimethyltin free group is treated with one atomic proportion of sodium in the solution it forms the corresponding sodium salt:

$$(CH_3)_3Sn + Na^+ + e^- \rightleftharpoons (CH_3)_3Sn^-Na^+$$

which is soluble and a light yellow color in liquid ammonia. According to Kraus and Sessions it is a good conductor in the solution. When an equivalent trimethyltin iodide was added to the resulting trimethyltin sodium the free group again settled to the bottom of the tube. In concluding, trimethyltin hydroxide is a fairly strong base since it ionizes to form $(CH_3)_3Sn^+$ and OH^- in liquid ammonia solution. The positive ion group $(CH_3)_3Sn^+$ is reduced by the electron into the neutral $(CH_3)_3Sn$ which is insoluble in the solution. However, along with the addition of an excess of sodium, the group dissolves in the solution again, for the group becomes electrically charged, due to the electron, forming the salt of $(CH_3)_3SnNa$.

Summary.

(1) General method of reduction of compounds in liquid ammonia by alkali metals and apparatus were described.

(2) Trimethyl stannyl iodide from methyl iodide and sodium-tin alloy and from which trimethyl stannyl hydroxide was prepared.

(3) Trimethyl stannyl free radical was prepared by the reduction of trimethyl stannyl hydroxide with metallic sodium in liquid ammonia solution.

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(1) Kraus and Bullard, *J. Am. Chem. Soc.*, **48** (1926), 2131.